Notes

Free Electron Model for Pyrazine & 1-3,5-Triazine

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The free electron model for the pi-electron system in benzene has been extended to pyrazine and 1,3,5-triazine, introducing an angular perturbation; calculated spectral transition and other physical characteristics have been found in good agreement with those obtained by LCAO-MO method.

IN an earlier paper from our laboratory[1] the free electron model using a modified Rudenberg and Parr[2] potential has been successfully extended to azabenzene, pyridine and the physical properties were calculated with encouraging results. In the present paper a number of physical properties for two other azabenzenes, viz. pyrazine and 1,3,4-triazine have been calculated on the basis of free electron model.

Method—From the generalized potential (Eq. 1) in terms of the coordinates of the centre of symmetry,

$$V = V(r,0) + V_0 \cos^2 p\phi \qquad \ldots(1)$$

potentials for pyrazine and 1,3,5-triazine are obtained by substituting $p = 1$ and $p = 3/2$ in Eq. (1), where p determines the position of nitrogen atom.

We have already described the solution for the smeared field problem[3] ($V_\phi = 0$). The eigen values and the eigen functions are given by Eqs. (2-5).

$$E_z = \left(n_z + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{m}} \qquad \ldots(2)$$

where $n_z = 1,3,5$ for pi-electrons.

$$E_\rho = (n_\rho + 1)\frac{h^2}{8\pi^2 mR^2\alpha} \qquad \ldots(3)$$

where $n_\rho = 0,\ 2,\ 4,\ldots$.

$$E_\phi = \frac{h^2}{8\pi^2 mR^2} l^2 f(\alpha^2 l^2) \qquad \ldots(4)$$

where $l = 0,\ \pm 1,\ \pm 2,\ldots$.

$$\text{with } 1 + 2\alpha^2 l^2 f(\alpha^2 l^2) = \sqrt{1 + 4\alpha^2 l^2} = 2\alpha\eta \qquad \ldots(5)$$

$$\Psi_{1,0,\pm l} = N\sqrt{K}ze^{-Kz^2/2}(\sqrt{C}\rho)^\eta\, e^{-C\rho^2/2}\, e^{il\phi}$$

where $K = \sqrt{\dfrac{4\pi^2 mk}{h^2}}$

and $C = \dfrac{1}{2R^2\alpha}$

Applying V_ϕ as perturbation, the ground state wave function as calculated[1] is given by Eq. (6)

$$\Psi_{1,0,\pm l} = N\sqrt{K}ze^{-Kz^2/2}(\sqrt{C}\rho)^\eta e^{-C\rho^2/2}\left\{e^{il\phi} - \frac{2V_0\pi^2 mR^2\alpha}{h^2} \times\left(\frac{e^{i(l+2p)\phi}}{\eta_l - \eta_{l+2p}} + \frac{e^{i(l-2p)\phi}}{\eta_l - \eta_{l-2p}}\right)\right\} \qquad \ldots(6)$$

and the associative eigen value is given by Eq. (7)

$$E_\phi = \frac{h^2}{8\pi^2 mR^2}\frac{1}{2\alpha^2}(2\alpha\eta_l - 1) + \frac{V_0}{2} + \frac{V_0^2\pi^2 mR^2\alpha}{2h^2} \qquad \ldots(7)$$

leaving E_z and E_ρ unaffected. Here it is also evident that the energy levels remain degenerate and are characterized by integral l-values.

The values of the parameters α and V_0 are taken as 0·25 and −1·7 eV respectively as in the case of pyridine[1].

Ground state dipole moment — The ground state dipole moments of pyrazine and 1,3,5-triazine are zero as calculated from the ground state eigen function using the relation (8)

$$\mu_x = \langle \Psi_0 \,|\, ex \,|\, \Psi_0 \rangle \qquad \ldots(8)$$

Static polarizabilities — Like pyridine the transition $|l| = 1$ to $|l| = 2$ is also allowed in the case of pyrazine and 1,3,5-triazine, so they are also basically two level systems. The pi-electron polarizability is then given by the expression (9)

$$\alpha_{ll'} = 2e^2\frac{\langle \Psi_l \,|\, x \,|\, \Psi_{l'}\rangle\langle \Psi_{l'} \,|\, x \,|\, \Psi_l\rangle}{E_{l'} - E_l} \qquad \ldots(9)$$

where $|l'|$ and $|l|$ are 2 and 1 respectively.

Only two components of polarizability α_{xx} and α_{yy} will exist and are given by Eq. (10)

$$\alpha_{xx}(yy) = \frac{2e^2\pi^2\left[1 + \dfrac{4V_0^2\pi^4 m^2R^4\alpha^2}{h^4}\left\{\dfrac{1}{(\eta_1 - \eta_2)(\eta_2 - \eta_3)} + \dfrac{1}{(\eta_1 - \eta_2)(\eta_2 - \eta_1)} + \dfrac{1}{(\eta_1 - \eta_0)(\eta_2 - \eta_1)}\right\}\right]}{E_{l'} - E_l} \qquad \ldots(10)$$

where the + sign should be taken with α_{xx} and − sign for α_{yy}. The calculated values of α_{xx} and α_{yy} for pyrazine and 1,3,5-triazine are given in Table 1.

These values are comparable with those calculated for pyridine[1].

The expressions for the first and second hyperpolarizabilities[4] are given by Eqs. (11) and (12) respectively

$$\beta = \sum_{i,j\neq 0}\frac{\langle\Psi_0|H'|\Psi_i\rangle\langle\Psi_i|H'|\Psi_j\rangle\langle\Psi_j|H'|\Psi_0\rangle}{(W_i - W_0)(W_j - W_0)} - \sum_{i\neq 0}\frac{\langle\Psi_0|H'|\Psi_0\rangle\langle\Psi_0|H'|\Psi_i\rangle\langle\Psi_i|H'|\Psi_0\rangle}{W_i - W_0} \qquad \ldots(11)$$

TABLE 1

	10^{+24} α_{xx} (cm³)	10^{+24} α_{yy} (cm³)
Pyrazine	2·6956	0·2956
1,3,5-triazine	3·5102	3·5102

TABLE 2 — NON-VANISHING β AND γ COMPONENTS IN PYRAZINE AND 1,3,5-TRIAZINE

(Values in esu)

$10^{+30}\ \beta_{xxx}$	$10^{+30}\ \beta_{xyy}$	$10^{+36}\ \gamma_{xxxx}$	$10^{+36}\ \gamma_{yyyy}$	$10^{+36}\ \gamma_{xxyy}$
PYRAZINE				
0·0000	0·0000	−86·6236	−86·0165	−28·7723
1,3,5-TRIAZINE				
−1·1688	−1·1688	−74·7640	−74·7640	−24·9207

$$\gamma = \sum_{i,j,k\neq 0} \frac{\langle\Psi_0|H'|\Psi_i\rangle\langle\Psi_i|H'|\Psi_j\rangle\langle\Psi_j|H'|\Psi_k\rangle\langle\Psi_k|H'|\Psi_0\rangle}{(W_i-W_0)^2(W_j-W_0)} \quad \ldots(12)$$

In these expressions H' stands for *ex*, *ey*, *ez*. Like pyridine the first hyperpolarizability for pyrazine and 1,3,5-triazine also exist and is given by the second term of the expression (11). From our estimated[3] $\langle\Psi_l|\,x\,|\,\Psi_{l'}\rangle$ and $\langle\Psi_l\,|y|\,\Psi_{l'}\rangle$ the non-vanishing β and γ components for pyrazine and 1,3,5-triazine have been calculated and are given in Table 2.

Pi-electron susceptibility and pi-quadrupole moment — The pi-electron susceptibility[5] and the pi-quadrupole moments[6] calculated from the relations (13 and 14)

$$\chi_{mol} = -\frac{Ne^2}{6mC^2}\sum \bar{r}^2 + \frac{Ne^2}{6m^2C^2}\sum \frac{|P(n,n')|^2}{h\nu(n',n)} \quad \ldots(13)$$

and

$$Hzz = \sum_i e_i r_i^2\ P_2\,(z_i/r_i) \quad \ldots(14)$$

for pyrazine and 1,3,5-triazine are equal.

The dia- and paramagnetic terms obtained are $-57{\cdot}54\times10^{-6}$ and $35{\cdot}09\times10^{-6}$ respectively and the calculated value of the pi-quadrupole moment for the two moles is $11{\cdot}4784\times10^{-26}$ esu. These values are comparable with those calculated for pyridine[1]. As we have no experimental data to compare with these results it is difficult to say how far these results are correct.

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Liquid Crystalline Behaviour of Some Schiff Bases Derived from 4-*n*-Alkoxy-1-naphthaldehydes & *p*-(*n*-Amyloxy)aniline

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Five compounds of the homologous series 4-*n*-alkoxy-1-naphthylidene-*p*-(*n*-amyloxy)anilines have been synthesized and their liquid crystalline behaviour studied. The C_1-, C_3- and C_5-homologs are non-mesomorphic. The C_2-homolog is monotropic nematic in nature while the C_4-derivative exhibits enantiotropic nematic mesophase. The C_2- and C_3-homologs exhibit two solid modifications. The metastable modification has a transition temperature lower than that of the stable modification.

SYNTHESIS of low melting liquid crystalline compounds has aroused considerable interest recently in view of the potential applications of the compounds. Liquid crystalline substances comprise linear and rigid molecules. It is found that when molecular structure is varied, the liquid crystalline properties also change markedly. Dave *et al.* have observed that the introduction of a 1,4-substituted naphthalene moiety into a mesomorphic compound considerably reduces the liquid crystallinity of the compound[1,2]. Here we present the results of our studies on the mesomorphic behaviour of some members of the homologous series 4-*n*-alkoxy-1-naphthylidene-*p*-(*n*-amyloxy)anilines. Five Schiff base compounds (C_1-C_5) of the series were prepared by condensing various 4-*n*-alkoxy-1-naphthaldehydes[1] with *p*-(*n*-amyloxy)aniline[3]. The mesomorphic behaviour of these compounds was studied using a Leitz Ortholux II polarizing microscope equipped with a Leitz heating stage. The analysis for C, H and N for these compounds agreed well with the calculated values. The melting points and transition temperatures of these compounds are given in Table 1.

The C_1-,C_3- and C_5-homologs are non-mesomorphic. The C_2-member is monotropic nematic in nature while the C_4-derivative exhibits enantiotropic nematic mesophase. The C_2- and C_3-homologs exhibit two solid modifications C_I and C_{II}; the stable modification C_I has the higher transition point than

TABLE 1 — TRANSITION TEMPERATURES OF 4-*n*-ALKOXY-1-NAPHTHYLIDENE-*p*-(*n*-AMYLOXY)ANILINES

Alkyl group	Transition temp.* (°C)	
	Nematic	Isotropic
CH_3	—	86·5
C_2H_5	(61·5)	81·5[a], 74·5[b]
C_3H_7	—	78·0[a], 68·0[b]
C_4H_9	62·5	64·5
C_5H_{11}	—	68·5

*Figure in parenthesis indicates monotropy (a) stable modification, and (b) metastable modification.